Mixed Conductivity in Nanocrystalline Oxide Thin Films

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The physics of phenomena occurring in nanocrystalline systems is related to spatially confinement effects, which can lead to qualitatively changes in the electrical transport, lattice dynamics, optical and catalytic properties. A number of studies has shown that some fundamental properties of nanocrystalline materials can be significantly enhanced by controlling their grain size in the range less than 100nm. These effects are attributed to grain boundary and grain size-dependent defect equilibria, which can influence nonstoichiometry. The ability to enhance properties by controlling the microstructure has created a new challenge for ion conductors and may impact a number of applications including gas sensors, fuel cells and ionic membranes where enhanced electrical properties and reaction kinetics are the most important aspect.

This presentation will summarize recent results obtained in a study of the influence of microstructure on the electrical and optical properties of nanocrystalline acceptor - doped $ZrO2$ and $CeO2$ thin films. These materials are exceptional oxygen conductors and for many applications it is very important to evaluate the relationship between electronic and ionic conductivities and the nonstoichiometry which is controlled by oxygen activity, impurities and microstructure.

Specimens of $ZrO2$:(Sc,Y), $CeO2$ and $CeO2$:Gd were obtained by the polymeric precursor spin coating technique, which has been proved to be particularly useful for the formation of dense nanocrystalline thin films with very uniform microstructure, which can be controlled in the grain size range of 1 - 400nm depending upon the annealing temperature. A variety of characterization techniques including x-ray diffraction, EXAFS, impedance spectroscopy and Raman scattering have been used for the evaluation of nanocrystalline material properties.

The electrical conductivity was studied by impedance spectroscopy as a function of temperature and oxygen activity. The results have been interpreted in a model in which defect associates were considered. From this the electronic and ionic conductivities were determined and correlated with the microscructure. Examples are given, which illustrate enhancement of both ionic and electronic conductivities. It has been found that the electronic conductivity of $ZrO2$:Sc is about 4 orders of magnitude higher (at 900oC) than that observed for $ZrO2$:Y and dominates the total conductivity in reducing atmosphere. This observation correlates with the nature of Sc which forms a donor level in the order of 0.9eV below the conduction band compared to 2eV for $ZrO2$:Y specimens. For $CeO2$ when the grain size enters the nanocrystalline regime, an enhancement in electronic conductivity has been observed , which appears to be related to a decrease in the enthalpy of oxygen vacancy formation. In the case of $CeO2$:Gd and $ZrO2$:Y, the electrical conductivity of nanocrystalline specimens has extrinsic character and is attributed to ionic transport. An increase of the ionic conductivity is observed which is probably due to reduction of the activation energy for ion mobility.

The nonstoichiometry of nanocrystalline materials has also been studied by Raman spectroscopy. The spectra have been described using the spatial correlation model from which the oxygen defect concentration has been determined and correlated with microstructure. A direct comparison has been achieved between the electrical conductivity and quantum confinement effects observed for nano- and microcrystalline specimens by Raman spectroscopy and correlated with a defect model.

The results showed that the defect equilibria of nanocrystalline oxides are related to the microstructure and the type of acceptor impurities. The overall conclusion to which one arrives is that the electrical and optical phenomena that are currently being observed in nanocrystalline materials can be effectively controlled by understanding their relationships to the microstructure. The ability to use nanocrystalline oxide thin films for gas sensors and fuel cells will be highlighted and their advantages will be discussed.

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